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IMPROVEMENT OF CORROSION-WEAR BEHAVIOUR OF MATERIALS BY NOVEL SURFACE TREATMENT TECHNIQUES

H. HINDAM
CORROSION SCIENCE SECTION

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by

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ABSTRACT

Novel surface treatment techniques, including ion implantation, laser treatments and plasma spray are described briefly. The beneficial effects of such treatments on the high temperature corrosion and wear behaviour of materials are discussed, and several illustrative examples are given. Further potential applications of these techniques for the surface engineering of corrosion-wear resistant alloys are suggested.

LABORATOIRES TECHNOLOGIQUE DES METAUX
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AMÉLIORATION DU COMPORTEMENT DES MATÉRIAUX FACE A LA CORROSION ET L'USURE PAR DES NOUVELLES TECHNIQUES DE TRAÎTEMENTS DES SURFACES

par

H. Hindam

RÉSUMÉ

Les techniques récentes pour le traîtement des surfaces des matériaux, incluant l'implantation des ions, traîtements avec LASER et projection par plasma ont fait l'objet d'une brève revue. L'effet de ces traîtements sur le comportement des matériaux face à la corrosion à hautes températures et l'usure est discuté. Des applications futures de ces techniques pour la synthèse de surfaces résistantes à la corrosion et l'usure sont suggérées.

INTRODUCTION

Materials resistance to corrosion and/or mechanical wear is a prime requisite for many engineering applications. In particular, materials are being subjected to increasingly aggressive environments as higher temperatures are sought to improve the efficiency of many processes, as low-grade fuels are utilized and as more stringent environmental protection regulations are enforced. This is particularly so, in the new technologies for burning and converting fossil fuels (e.g., fluidized bed combustion of coal or oil shales, coal-driven utility turbines, jet turbines, etc.),

Research has shown that alloys originally developed to combine high temperature mechanical strength and fabricability with acceptable resistance to corrosion in O_2-rich gases, are not adequate for application in these emerging technologies. Several factors are responsible for the rapid degradation of these alloys: low oxygen partial pressure, harmful gaseous species containing S, C, Cl, etc., scale disruption because of mechanical and/or chemical wear by particle-laden fluids, molten salts or slags. In addition, commercial alloys contain certain impurities which are detrimental to corrosion behaviour in complex environments. These conditions inhibit the formation of protective oxide films, and non-protective sulphide or carbide phases are formed instead. For example, nickel-containing alloys often fail catastrophically because of the formation of a low melting Ni-NiS eutectic.

Thermal treatments can be used to incorporate certain elements into the alloys to improve their resistance to oxidation (Cr and Al) and wear (B,N,C). Since these processes are controlled by solid-state diffusion, they are time consuming and require high temperatures. A subsequent heat treatment is necessary to restore the mechanical properties of the alloys.

Novel techniques, involving surface treatments with electron, ion, laser or plasma sources (1-7), provide unique opportunities to improve alloy corrosion-wear behaviour by tailoring the surface composition and microstructure. Because these treatments are carried out at room temperature, the bulk properties are not altered. In addition, novel materials can be produced with unique compositions and structures, otherwise inaccessible by thermal routes.

As part of a recent programme on advanced materials and fabrication technologies, the Canada Centre for Mineral and Energy Technology (CANMET) is

investigating the potentials of novel surface modification techniques, with emphasis on ion and laser treatments as well as plasma spraying, in the synthesis of novel materials with improved properties and superior performamce. The objective of this report is to review and explore the potential of these techniques to improve the corrosion-wear behaviour of materials at high temperatures.

This review includes a brief description of the instrumentation, the effect of the operating parameters and a summary of advantages and limitations. Finally, the application of these techniques to improve the high-temperature corrosion and wear behaviour of materials is discussed.

1. ION IMPLANTATION (8-12)

1.1 THE PROCESS AND OPERATING PARAMETERS

A simplified schematic of an ion implantation system is given in Fig. 1. The system consists of an ion source, an analyzer magnet, an acceleration column and a work station, kept under moderate vacuum. Ions, accelerated in an electric field to energies of up to a few keV, bombard the surface of the substrate. They collide with substrate atoms and come to rest, assuming a Gaussian distribution, around a mean depth of $\sim$0.1 μm. Atomic interaction results in physical damage including the formation of vacancies, interstitials, dislocations, etc.

For a given implant/substrate system, the concentration profile is influenced by two factors: (i) the acceleration voltage, which determines the mean penetration depth and (ii) the current density and implantation time, i.e., the implantation dose (atom/cm^2). It is this parameter that determines the actual concentration.

1.2 ADVANTAGES

i) Flexibility

The extent to which the implanted ions interact with the substrate depends on their kinetic energy only. Thus, ion implantation is not subject to any thermodynamic constraints: any ion can be implanted in any substrate, solid solubility limits can be exceeded and metastable phases can be formed. However, metastable phases may revert rapidly to their stable forms upon heating, diffusion being enhanced by the high concentration of defects induced by ion bombardment.

ii) No Adhesion Problems

A major problem encountered in most surface treatment techniques is the bonding between the treated layer and the substrate. In ion implantation, however, the implanted species are incorporated in the "host" lattice with no defined boundaries between them. Adhesion problems are therefore avoided.

iii) No Dimensional Changes

Ion implantation does not produce any dimensional changes or distortion in the substrate. Therefore, no additional steps are needed to meet tolerances or improve surface finish.

1.3 LIMITATIONS

i) High Cost

Capital cost for a laboratory-scale unit is in the range \$300K-\$1000K. The operating cost is estimated at \$10/cm^2. Prototypes of powerful machines for industrial applications have been built with the following specifications: beam current 10-20 mA/cm^2, acceleration voltage 100-500 kV, beam-size 1000 cm^2. Such machines require a significant capital investment.

ii) Shallow Penetration Depth

Although ion implantation is a shallow treatment process, beneficial, long-lasting effects can be obtained in certain applications. Specific examples will be discussed later.

iii) Limited Amount of Implanted Species

The maximum obtainable implant concentration is limited by the ejection of atoms from the substrate (sputtering). A dynamic state of equilibrium is reached when the rate of implantation equals the rate of sputtering. Peak concentrations of implanted ions can range from 0.1 to 30 wt %.

iv) Line-of-sight process

Ion implantation is inherently a line-of-sight process. This shortcoming can be overcome by a suitable manipulation of components with complex shapes during ion implantation or by using multiple ion sources.

2. LASER TREATMENT (13-18)

2.1 THE PROCESS AND THE OPERATING PARAMETERS

A laser beam is brought to focus near the surface of the workpiece. To obtain a full coverage, the beam is rasted by mirrors and lenses, or by moving the workpiece on an X-Y raster table. The laser beam can be used to heat or melt the surface. Alloying is achieved by melting a pre-deposited layer or by injecting powder particles into the melted surface pool. Cladding of refractory particles can be achieved in the same way. To avoid oxidation of reactive metals, an inert-gas shroud (which also suppresses plasma formation) or a vacuum chamber is used. The cross section of a surface Fe-Cr alloy produced by laser alloying are included in Fig. 2.

Laser systems are classified according to the lasing medium (solid or gas) and mode of operation (pulsed or continuous). The systems which are useful for surface treatments are:

i) the Nd-YAG (neodymium-doped yttrium-aluminum-garnet) pulsed or continuous laser (wave length 1.06 μm) and

ii) the CO_2 continuous laser (wave length 10.6 μm).

Continuous gaseous lasers generate high power output (up to 25 kV) whereas the output of solid-state lasers is quite limited (2 kW, maximum).

The main control parameters in laser treatments are the incident power density and the interaction time. These two parameters determine the depth of the treated layer (typical range 0.1-0.5 mm).

2.2 ADVANTAGES

i) Rapid Cooling Rate

The main advantage of laser treatment is the ultra-high cooling rate (10^6-10^9 K/s) arising from very large temperature gradients combined with high rates of heat input and the high thermal diffusivity of the solid substrate which acts as a heat sink. Laser treatment may be regarded as a superficial rapid-solidification technique that can refine grain size and microstructure. If the alloy system is suitable metastable or amorphous phases can form. Under modest cooling rates (continuous laser, long interaction time), solidification of the molten layer can be influenced by the underlying substrate leading to a textured morphology.

ii) Good Bonding

Unlike the coatings produced by conventional plasma spraying, a good bond is achieved by laser treatments because melting ensures intimate mixing of the alloying material and the substrate near-surface region.

iii) Large Penetration Depth

The depth of the treated layer is at least one order of magnitude larger than that obtained by ion implantation.

iv) Precise Control

The laser beam can be focused down to a very small spot (~100 μm). This fine focus is very useful for applications requiring precise control over the area to be treated.

2.3 LIMITATIONS

i) Low Processing Rate

The rate at which a surface can be processed with the low-power pulsed laser is quite small. Higher rates can be achieved with a high-power continuous laser.

ii) Low Absorption by Metals

Laser radiation is readily absorbed by all materials except metals. The absorption of laser radiation by metals increases with decreased wavelength. Absorption also depends on surface finish. The high reflectivity of a metallic surface can be overcome by using higher incident energies or by coating with an absorbent material such as carbon, Mn or Zn-phosphate.

iii) High Surface Roughness

Laser-melted surfaces are inherently rough and rippled because of surface tension gradients and melt flow. Surface roughness is increased by the overlapping between passes that is necessary to ensure full coverage (Fig. 2). Operating lasers in the pulsed mode produce more surface roughness than in the continuous mode. A second pass smooths these irregularities but does not eliminate them. For some applications, however, surface roughness might be desirable; e.g. improving scale/coating-substrate adhesion.

iv) Capital Cost

The capital cost varies considerably with the laser output power. A 400 W Nd-YAG laser with a computer-operated handling system costs $200K; a 10 kW CW CO_2 laser costs $1000K.

v) Safety Provisions

The radiation emitted by some lasers (such as the CO_2 laser) falls within the invisible spectrum. The use of such lasers requires elaborate safety provisions.

vi) Line-of-Sight Process

As with ion implantation, laser-treatment is a line-of-sight process. However, beam rastering and/or work-piece handling systems eliminate this shortcoming.

3. PLASMA SPRAY (19-22)

3.1 THE PROCESS AND THE OPERATING PARAMETERS

The system consists of a plasma torch, powder and gas feeders, torch and workpiece handling systems. As illustrated in Fig. 3, the torch consists of a W cathode and a water-cooled Cu anode in the form of a nozzle. The plasma produced by the ionization of an inert gas under the impetus of an electrical discharge is accelerated to speeds up to 600 m/s. The powder is injected into the plasma and is both melted and accelerated. The molten droplets flatten and solidify the instant they impinge on the substrate. Because of the rapid solidification rate and a relatively low impingement rate, each flattened droplet solidifies independently; thus a lenticular multi-layered microstructure is produced. Such coatings are inherently porous; in practice, only 90% of the theoretical density is achieved. A typical microstructure of a plasma-sprayed FeCrAlY coating is given in Fig. 4.

The quality of the coating depends on the spray parameters and the powder characteristics. The spray parameters include: torch power(IV), types and flow rates of plasma gas and powder gas carrier, spray angle and distance, and torch design (particularly how the powder it injected into the plasma). Powder characteristics include: particle size and distribution, shape, density, heat capacity, thermal conductivity and feed rate. Because of the com-

plexity of the operating parameters, the optimum spraying conditions are determined experimentally. The optimum conditions are those which ensure that plasma energy and particle interaction with the plasma induce melting (without chemical decomposition) and maintain the particles in a molten state until they impinge on the substrate. Consistency in powder characteristics is necessary for good quality coatings.

Reactive powders are sprayed with either an inert-gas shroud to prevent ingress of air, or in a chamber filled with inert gas at low pressure. The latter process, referred to as low pressure plasma spray (LPPS) offers additional advantages over conventional atmospheric plasma spray. Thus:

i) plasma velocity is much higher, and produces denser deposits,
ii) a large beam increases coverage,
iii) if the substrate is heated residual stresses are reduced and adhesion is improved, and
iv) noise is reduced and particulate emission controlled.

3.2 ADVANTAGES

i) Flexibility

Metals, ceramics and some polymers can be plasma sprayed.

ii) Low Capital Cost

A conventional atmospheric plasma spray system with the basic peripherals (powder feeder and gas supply) costs less than $100K. However, a computer-assisted handling system for the torch and workpiece increases the price substantially. A LPPS system is much more expensive although, as discussed above, it offers several advantages.

iii) High Deposition Rate

iv) Thick Coatings

Typical coating thicknesses: 100-3000 μm. Free-standing deposits can also be produced.

3.3 DISADVANTAGES

i) Poor Adhesion

The adhesion between a coating and substrate is generally poor because only mechanical bonding is normally involved. A limited improvement in adhesion is achieved by increasing the substrate surface roughness, eg., by sand blasting. A significant improvement in adhesion is achieved by heating the substrate (thus promoting diffusion bonding) and/or by sputter-cleaning the surface by negatively biasing the substrate relative to the torch (19).

ii) High Porosity

As indicated above, plasma-sprayed coatings are inherently porous. Porosity can be sealed or reduced by a post-deposition process such as peening with glass beads, hot isostatic pressing, or laser glazing.

iii) Line-of-Sight Process

Similar to ion implantation, plasma spraying is a line-of-sight process which requires torch and workpiece handling systems to overcome this shortcoming.

iv) Noise and Particulate Pollution

Conventional atmospheric plasma spraying is very noisy and requires particulate exhaust and disposal systems.

4. IMPROVEMENT OF MATERIAL CORROSION BEHAVIOUR

In this section, the application of the techniques described above to improve the high temperature corrosion resistance of materials is discussed. Typical examples are given, and the underlying mechanisms responsible for the improvement are discussed. New potential applications are suggested.

4.1 FORMATION OF DIFFUSION-BARRIER FILMS

Alloy resistance to degradation in corrosive environments at high temperature depends on forming a slow-growing, adherent film, such as Cr_2O_3, Al_2O_3 or SiO_2. However, added to the alloy in sufficient quantities, Cr, Al or Si can be detrimental to mechanical properties. Thus, the prospect of circum-

venting this problem by surface alloying is attractive and such an approach would also conserve strategic materials.

In practice, ion implantation of Cr, Si or Al in pure metals (Fe or Ni) does not enrich the surface to a level sufficient for the selective and sustained growth of a protective scale (Cr_2O_3, SiO_2 or Al_2O_3) (23,26). The scales which did form on these alloys consisted of an imperfect oxide film rich in the implanted species together with large oxide nodules of the base metal. However, ion implantation of dilute binary or ternary alloys produced a significant improvement of oxidation behaviour. For instance, implantation of 10^{17} Al^+/cm^2 in an FeCrAl (1.4 wt % Al) alloy raised the surface Al concentration to 10 wt % and reduced the oxidation rate by a factor of 140 by forming of a continuous Al_2O_3 film (27). Although the oxidation experiments were carried out for a short duration (24 h), it is possible the beneficial effect may be long-lasting because the growth of the Al_2O_3 film may be sustained by Al diffusion from the alloy bulk to the scale/alloy interface.

In other work, incorporation of a high concentration of Si (up to 25 wt % in Fe) was achieved by ion-beam mixing which decreased oxidation rate by a factor of 50 by forming a protective SiO_2 film (24).

Laser treatment and plasma spraying offer more effective ways than ion implantation or ion-beam mixing for producing reasonably-thick surface alloys. Each technique has its own characteristics. Although plasma spraying is very flexible in the coatings it can form, the process has two inherent shortcomings: high porosity and poor adhesion. On the other hand, LPPS produces coatings which are more dense and well bonded to the substrate, but the process is expensive. A better and more economical approach is to use an inert-gas shrouded torch to spray composite powders (28) of constituents which react exothermically. The evolved heat contributes to melting, and the coatings are more dense and coherent. Ni/Al and Fe/Al generate significant amounts of heat from the heat of formation of the highly stable intermetallic compounds (29,30). The deposition parameters, particle size and composition of the composite powder must be optimized to ensure that the reaction is carried out to completion. High-temperature oxidation-resistant surface alloys based on the Fe-Cr-Al and Fe-Si-Al systems can be produced by this procedure.

Surface treatment techniques provide a flexible experimental approach to developing new oxidation-resistant alloys based on the addition of several stable oxide forming elements to form ternary (A-B-O) or more complex oxide phases. The total of such additions to form a continuous protective layer is probably less than that required of a single element.

4.2 MODIFICATION OF THE TRANSIENT GROWTH STAGE

Development of a barrier film is preceded by a transient stage during which the oxides/sulphides of all the alloy components compete for dominance (31). Such transient oxide as NiO, CoO, etc. play an important role in the attack of alloys by molten salts (32). The formation of sulphides, particularly those of Ni, Co and Fe, leads to catastrophic attack once the low eutectic temperatures of these metal-sulphide systems are exceeded (33).

Several processes occur during the transient growth stage: nucleation, lateral growth of nuclei and diffusion of alloying elements to the alloy surface. Surface treatments can influence these processes and possibly restrict the transient stage.

Surface defects, residual stress and increased surface roughness produced by ion bombardment influence the nucleation of oxides/sulphides (34). Preferential sputtering changes surface composition, and thus, the stability of phases. Radiation damage enhances diffusion and could lead to the rapid development of a protective film. Hence, ion bombardment affects the composition of an initial film, its microstructure (grain size and orientation) and its rate of formation.

Research on the effect of physical damage induced by ion bombardment on oxidation has been confined to pure metals. The effect was investigated (24) by implanting either inert gases or ions similar to the substrate (ion-self implantation). These treatments can decrease or increase oxidation rate by a factor ranging from 2 to 5 but studies need to be extended to alloys in a systematic way.

Laser surface melting refines the grain size and microstructure of multi-phase alloys. Thus, inclusions may be dissolved and remain in solution or reprecipitate with a different distribution as the surface solidifies. The refined microstructure will affect alloy behaviour during the transient stage because the high density of grain boundaries arising from the fine alloy grain size will enhance the diffusion of active elements and, thus, promote the rapid development of protective films.

Sputter-cleaning the substrate prior to plasma spraying improves coating adhesion significantly. The processes involved in this treatment and their effect on surface composition and microstructure are not well understood. The effect of similar treatments on the oxidation behaviour of coatings has not been investigated. It is probable that such treatments could affect both the transient and later stages of growth and/or the adhesion of oxide films formed on such coatings.

4.3 MODIFICATION OF POINT-DEFECT CONCENTRATION

Doping non-stoichiometric compounds with alliovalent impurities can modify the concentration of intrinsic point defects, and hence, lattice diffusion (at high temperatures). The changes in defect concentration are governed by the Wagner-Hauffe rules which are based on the electroneutrality principle (31).

Although alloy concentrations which locally exceed solubility limits can be achieved by ion implantation, the absolute amount of an implanted species is small. Upon heating, the implanted species redistribute in the alloyor scale exerting a negligible effect on growth because of low local concentrations.

4.4 BLOCKAGE OF SHORT-CIRCUIT PATHS

It is well established that structural defects (e.g., grain boundaries, dislocations, etc.) play an important role in the growth of scales at low and intermediate temperatures (35,36). For instance, based on tracer diffusion measurements in oxides and the kinetics of oxide film growth on metals, it was deduced that the ratio of grain boundary and lattice diffusion coefficients can be as high as 10^6 in the case of NiO (36), 10^4 in the case of ZrO_2 (36), and 10^2 in the case of Al_2O_3 (37).

The addition of small amounts ($\sim$0.1 wt %) of oxygen-active elements (e.g., Y, Ce, etc.) or a dispersion of the oxides of these elements in Cr_2O_3-forming alloys reduced the growth kinetics of a surface film by one to two orders of magnitude (38). These additions also significantly improve scale adhesion (see below). It has been suggested (39) that the growth rate of Cr_2O_3 films is reduced by the segregation of coherent micro-precipitates (e.g., Y_2O_3, CeO_2, etc.) at grain boundaries and dislocations, effectively inhibiting the outward diffusion of Cr along these short-circuit paths. The

segregation of "over-sized" atoms to within a few nm of grain boundaries in a variety of systems was confirmed by Auger electron spectroscopy (40).

In p-type cation conductor oxide, such as NiO, it is probable that, in addition to the mechanism described above, over-sized ions, such as Y^{+++} or Ce^{++++}, can act as vacancy trapping sites, effectively reducing the mobility of vacancies.

The implantation of strong oxide forming elements at doses of $\sim 10^{17}$ ions/cm^2 in Cr_2O_3-forming alloys was found to have similar effects, lasting ~5000 h (maximum exposure period), to those of direct alloying (24). The effectiveness of ion implantation despite its low mean concentration probably occurs as a result of high local concentrations of the implanted species at defect sites (24).

4.5 IMPROVED SCALE ADHESION

Minor additions (0.1 ~ 0.3 wt %) of certain oxygen active elements (Y, Hf, Ca, Ce, etc.) remarkably improve the adhesion of Cr_2O_3 and Al_2O_3 scales (38,41). Consequently, alloy performance under thermal cycling is also significantly improved.

These small additions induce significant changes in the scale composition and its microstructure. They act by reducing grain size, increasing microporosity, producing a tortuous alloy/scale interface which is otherwise planar on a micro-scale, and eliminating cavities at this interface. A dispersion of oxides of the active elements (e.g., Y_2O_3, $YCrO_3$, etc.) is found in the scales in the form of individual grains, grain boundary phase, or stringers. The active elements can also dissolve in the scale or segregate at the alloy/scale interface.

The improved adhesion could be caused by residual tensile stresses associated with over-sized atoms, relief of growth and athermal stresses, superior mechanical strength and/or enhanced ductility of the scale, and increased bond strength between the scale and the alloy. Although several interpretations (38) based on these principles have been advanced, a thorough understanding of how microstructural modifications brought about by minor additions influence mechanical and adhesive properties of thin films has yet to be achieved.

Ion implantation offers a unique research tool for adding various elements to an alloy in a controlled way to study their effects on scale growth, microstructure and adhesion. Research so far has demonstrated that the implantation of Y and Ce at a dose of $\sim 10^{17}$ ions/cm^2 in Cr_2O_3 and Al_2O_3-forming alloys can improve scale adhesion to a point comparable to direct alloying (23,24,27).

The effectiveness of some beneficial elements (e.g., Y, Ca, etc.) is limited by their low solubility when directly alloyed. Surface treatment techniques would be particularly useful in incorporating such elements in alloys.

4.6 MODIFICATION OF ELECTRONIC CONDUCTIVITY

Scale growth is controlled by the migration of ions and the counter-current flow of electrons or positive holes. Therefore, if the electronic conductivity is modified there should be corresponding changes in scale growth. Ion implantation may influence electronic conductivity by interaction with electrons (or positive holes) and influence their mobility. The potential for controlling scale growth through this mechanism has not been explored.

4.7 THERMAL BARRIER FILMS

Materials performance can be improved by applying protective coatings. An example of this approach is the use of thermal barrier coatings in the cylinder liners of diesel engines, and blades of jet turbines (42). Indeed, the use of such coatings improves engine performance by reducing heat losses and permitting higher combustion temperatures. Partially stabilized ZrO_2 is the most commonly used thermal barrier coating. It is partially stabilized by additions of CaO, MgO, or Y_2O_3.

In addition to good thermal insulation, thermal barrier coatings must have two other essential properties: resistance to corrosion and thermal shocks. Corrosion resistance is imparted by a NiCrAlY layer which also promotes the bonding between the substrate and ZrO_2. Resistance to thermal shock is increased by the presence of microcracks and high porosity. The phase transformation of ZrO_2 (cubic-tetragonal-monoclinic-crystal structures) induces microcracking because of differences in the specific volumes.

Plasma spraying produces castings that are inherently porous, and therefore, are good thermal barriers. Laser shock treatment can be used to control the distribution and orientation of microcracks in a coating, thus enhancing resistance to thermal shock (43).

5. IMPROVEMENT OF MATERIALS WEAR BEHAVIOUR

The mechanical wear of materials occurs by different modes: abrasion, erosion, adhesive wear and fretting. Abrasion and erosion are the most common mechanical degradation mechanisms in energy utilization and conversion systems. Abrasion is caused by particles which slide and roll on a surface, whereas erosion is caused by the impingement of particles carried by a fluid (liquid or gas) or the collapse of vapour bubbles on a surface.

Because material loss occurs by plastic deformation and microfracture, increased hardness and toughness usually improve resistance to mechanical wear. In particular, data compiled from a variety of experiments show that abrasion rate is reduced by several orders of magnitude if the surface hardness of a material exceeds that of the abrasive particles (44).

In the following sections, examples are given to illustrate the beneficial effects of surface treatment, and the mechanisms responsible for improvement are discussed.

5.1 RESIDUAL STRESSES

Generally, ion bombardment results in a work-hardened surface because of the lattice disorder created by the displacement of atoms (24,26). In particular, residual stresses are induced in the surface layer by the implantation of large-size atoms (e.g., argon). The strain field associated with oversize "impurity" atoms interferes with the mobility of dislocations. However, because of the shallow implantation depth, the effect is not lasting.

5.2 SOLID SOLUTION HARDENING

Interstitial solid solution hardening is more effective than substitutional hardening. Interstitial atoms segregate at dislocations, pinning them down. Typical examples include the implantation of N in steel and in Ti (45-47). A more effective procedure is to implant substitutional-interstitial atom pairs, e.g., (N-Y) in steel and (N-Sn) in Ti (46). In the case of

N-implantation in steel, the improvement in wear resistance lasted even after the removal of a layer more than one order of magnitude deeper than the original implantation depth (26,46). Chemical analysis of samples tested at room temperature on a pin-on-disk wear assembly revealed than N was present at a depth which exceeded that of implantation. Apparently, friction-induced temperature increases are sufficient to cause the inward migration of N.

5.3 DISPERSION HARDENING

Typical examples of hardening by the formation of a dispersion of fine coherent precipitates include: implantation of N in Cr or Ti to form nitrides and implantation of Ta in steel to form carbides (45-48). This surface hardening procedure would be less effective than solid solution hardening because no autogenous mechanism could prolong its effect.

5.4 FORMATION OF A HARD AMORPHOUS LAYER

The implantation of Ti in steel significantly improves wear resistance by forming an Fe-Ti-C hard amorphous layer (45,46). Similar improvement was obtained by implanting other strong carbide formers (e.g., Ta, Mo, Nb, etc.). A hard, amorphous B-N coating was obtained by simultaneously implantating B and N (ion-beam mixing) (45,46).

Laser alloying is particularly useful for producing hard amorphous coatings because of the ultra-high heat input and quenching rates. Several systems based on Fe-metalloid (B, Si and P) have been investigated (18).

5.5 FORMATION OF A LAYER WITH A REDUCED COEFFICIENT OF FRICTION

MoS_2, a solid lubricant, reduces the coefficient of friction and thus reduces wear rate. This compound can be formed by the dual inplantation of Mo and S (26). Similar effects can be obtained by implanting soft metals (e.g., Pb, Sn, etc.). In an oxidizing environment, the wear rate of Y-implanted steel is significantly reduced because a fine-grained adherent Y_2O_3 film forms (23,26).

The concept of applying a film of solid lubricant can be extented to laser alloying and plasma-spray techniques.

5.6 PHASE TRANSFORMATION HARDENING

Because of the ultra-high quenching rates that attend laser heat treatments, the surface of steels can be hardened by the formation of martensite where applicable, (49,50). This surface heat treatment which causes no distortion is economically attractive.

5.7 MICROSTRUCTURAL MODIFICATION

Laser melting offers a flexible technique to control and modify the microstructure of alloys with the objective of increasing surface hardness to improve the wear resistance. Depending on the process parameters, a wide variety of microstructures can be obtained. This is an active research area which has not been fully exploited yet.

5.8 CERMET COATINGS

Laser treatments and plasma spraying produce relatively thick cermet coatings which combine hardness and toughness (51-54). Hard materials include the carbides, nitrides, borides, oxides and silicides of refractory metals (e.g., Ta, Ti, Mo, W, etc.). Cobalt-based alloys are often used as a binder on high value added components because of their high hardness relative to other alloys.

The size of the hard particles in a cermet and their volume fraction relative to the particle size of an impinging abrasive are the important factors which determine the wear resistance of a cermet (55). The wear rate decreases linearly with volume fraction of the hard particles in the coating. Small abrasive particles can initiate cracks at the interface with the alloy matrix enhancing the wear rate by spalling particles from the coating.

Although plasma spray offers greater flexibility than laser treatments in depositing wear-resistant coating because the rate of surface coverage is higher and a larger volume fraction of hard particles can be incorporated in the coating, the decomposition of refractory compounds (e.g., Si-C, W-C) is a major problem. Sufficient consolidation of the coating can be achieved in laser cladding by limiting the heat input to melt the binder alone.

CONCLUDING REMARKS

Novel surface treatment techniques offer a broad spectrum of opportunities to improve the corrosion-wear behaviour of surfaces without altering desirable bulk properties.

Because of the shallow affected depth and the limited amount of foreign substance which can be introduced into the substrate, ion implantation will be limited to applications which are quite sensitive to composition such as abrasive wear and mechanical behaviour of scales. Capital and operating costs are somewhat prohibitive to a wide commercial exploitation. However, ion implantation is considered as a unique investigative tool for studying the effects of minor additions on surface-sensitive properties.

Laser treatments and plasma spraying offer a wide flexibility in microstructural control and the deposition of a wide variety of materials, respectively. They may be regarded as complementary techniques for the optimization of the compositions and microstructures of surfaces. The major shortcoming of both techniques is the lack of throwing power; however, this has been largely overcome in advanced systems by utilizing computer-assisted handling systems.

Research and development must be directed toward the engineering of materials which offer a combined resistance to high-temperature corrosion and mechanical wear, two indispensible requirements in most of the advanced materials processing and energy utilization systems. Potential systems, including a wide variety of alloys and cermets, which may meet these two requirements, are being investigated.

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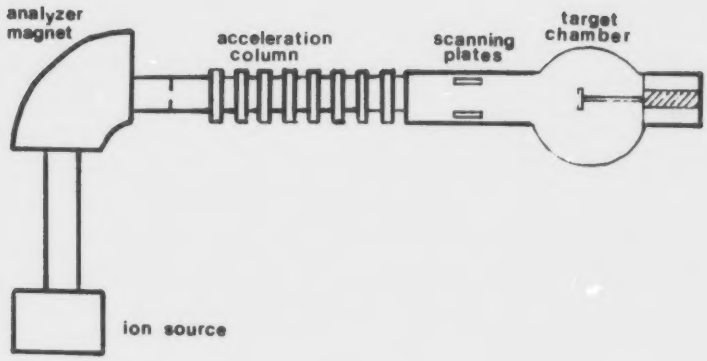

Fig. 1 Schematic of ion beam processing system. (neg 14670)

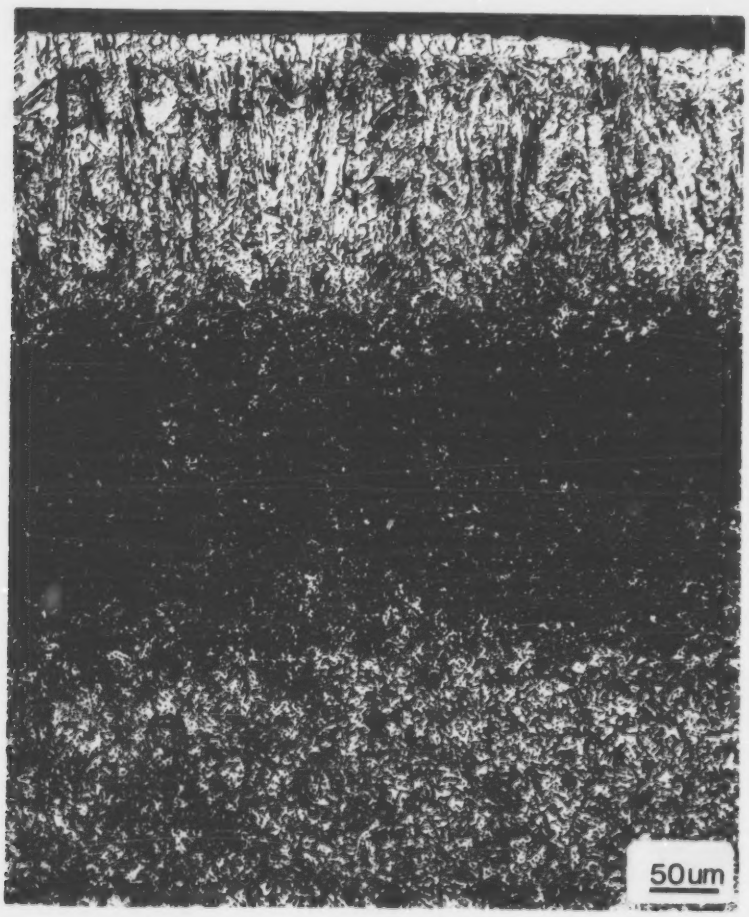

Fig. 2 Typical microstructure of a surface FeCr alloy produced by laser alloying

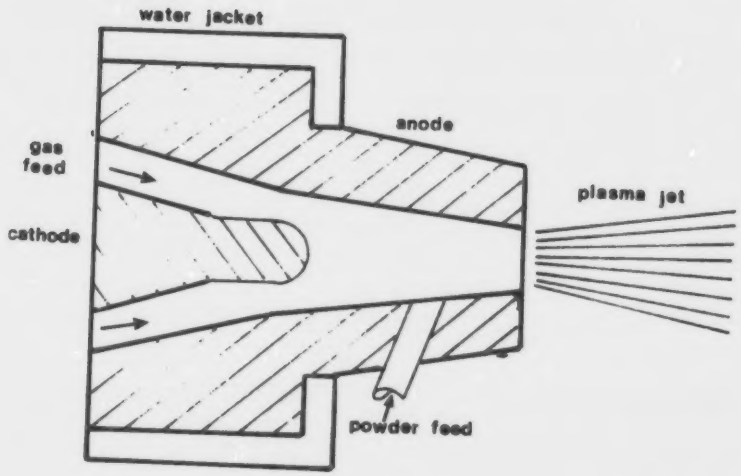

Fig. 3 Schematic of a plasma torch. (neg 14671)

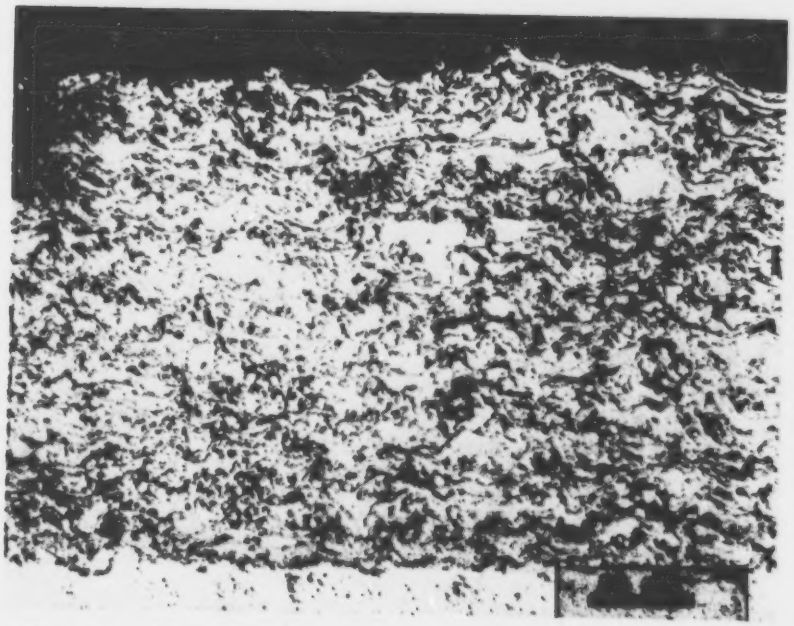

Fig. 4 Typical microstructure of a plasma-sprayed FeCrAly coating